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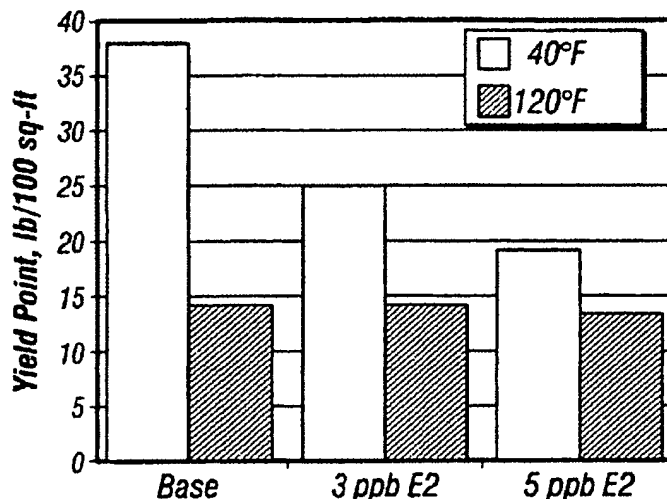
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(54) Title: THINNERS FOR INVERT EMULSIONS



(57) Abstract: A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said drilling fluids or well service fluids a thinner having the formula:  $R-(C_2H_4O)_n(C_3H_6O)_m(C_4H_8O)_k-H$  where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

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## THINNERS FOR INVERT EMULSIONS

### Background of the Invention

#### 1. Field of the Invention

5 This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids, at temperatures at or below about 50 degrees  
10 Fahrenheit (about 10 degrees Centigrade).

#### 2. Description of Relevant Art

A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid  
15 include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

20 A drilling fluid typically comprises water and/or oil or synthetic oil or other synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in  
25 the fluid. Such dispersed water in oil is generally referred to as an invert emulsion or water-in-oil emulsion.

A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or  
30 fluid-loss control agents, viscosifiers or viscosity control agents, and alkali. Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

5 An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling operation. Moreoever, a drilling fluid must be sufficiently viscous to be able to  
10 suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

Thinnerers may be added to the drilling fluid or drilling mud systems before  
15 and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, problems with such prior art thinners may occur when using the drilling muds at  
20 low temperatures (temperatures at or below about 50°F (10° C)).

At such low temperatures, despite the use of known prior art thinners, oil based drilling fluids typically have high or increased viscosity, which may render the fluids unusable for drilling. After pumping into the wellbore, drilling fluids may undergo heating from the formation, depending on the depth of the  
25 wellbore and the temperature of the formation. For example, heating in the range of about 150° to about 250°F (about 66° to about 121°C) is not uncommon and subterranean temperatures as high as about 350°F (about 178°C), particularly in very deep wellbores, are known. The Arctic region, for example, is known to have very low surface temperatures but very high  
30 subterranean temperatures. Even more problematic are deepwater wells (i.e., typically wells below at least about 1500 feet), which subject drilling fluids to chilling from cold waters surrounding the riser as the fluid returns to the surface from the high temperature subterranean formation. Such chilling of oil

based drilling fluids typically increases their viscosity while such subterranean heating of oil based drilling fluids typically reduces their viscosity.

Preferably, thinners which reduce the viscosity of drilling fluids at low temperatures will not affect the viscosity of the fluids at high temperatures.

5 That is, in many cases, a thinner is desired that is capable of "selectively" influencing the rheology or particularly reducing the viscosity of oil-based drilling fluids only at lower temperatures, such as may be encountered at the ground surface of the wellbore, or in the riser surrounded by waters above a deepwater offshore well, for example.

10 Thinners and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further, drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore,  
15 such as high temperatures, high pressures, and pH changes.

A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising invert (water-in-oil) emulsions, which are expected to be used in or to encounter low temperatures in drilling operations. As used herein, unless  
20 indicated otherwise, "low temperatures" shall be understood to mean temperatures at or below about 50°F (about 10°C).

### **Summary of the Invention**

According to the method of the present invention, a compound is added  
25 to a water-in-oil or invert emulsion drilling fluid or well service fluid which reduces the viscosity of the drilling fluid or well service fluid at low temperatures or which enables or enhances the ability of the drilling fluid or well service fluid to maintain its viscosity at low temperatures. The compound, which may be generally called a "thinner," continues to have this effect on a drilling fluid or  
30 well service fluid in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations. Further, this compound does not significantly affect the viscosity of the emulsion at high temperatures.

The compound has the following formula:



- 5 where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

The invention also comprises the composition of a water-in-oil or invert  
10 emulsion drilling fluid or well service fluid containing this thinner compound.

#### **Brief Description of the Drawings**

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2 at different  
15 temperatures.

Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3 at different temperatures.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4 at different  
20 temperatures.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5 at different temperatures.

Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6 at different  
25 temperatures.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7 at different  
30 temperatures.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8 at different temperatures.

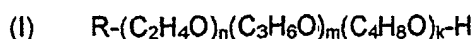
Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9 at different temperatures.

5 **Detailed Description of Preferred Embodiments**

The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of drilling fluids or well service fluids comprising invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing  
10 subterranean formations and has particular advantage in applications where the fluids are subjected to low temperatures, as in drilling or in servicing deepwater offshore wells. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and  
15 various additives. As the term is used herein, "invert emulsion" or "oil-in-water emulsion" is understood to mean the liquid portion of the drilling fluid comprising an emulsion (excluding solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

In the method of this invention, a composition or compound having the  
20 following formula (I) is added to the invert emulsion or oil-based drilling fluid (or well service fluid) to reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity at low temperatures. The compound may be added to the fluid during initial preparation of the fluid or later as the fluid is being used for drilling or well  
25 service purposes in the formation. The quantity added is an effective amount to maintain or effect the desired viscosity of the drilling fluid. For purposes of this invention, an "effective amount" of thinner of formula (I) is preferably from about 0.5 to about 15 pounds per barrel of drilling fluid or mud. A more preferred amount of thinner ranges from about 1 to about 5 pounds per barrel  
30 of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid.

Formula (I) is:



where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. Preferably, R has about 8 to about 18 carbon atoms; more preferably, R has about 12 to about 18 carbon atoms; and most preferably, R has about 12 to about 14 carbon atoms. Also, most preferably, R is saturated and linear.

The compositions or compounds of formula (I) may be prepared by customary techniques of alkoxylation, such as alkoxyating the corresponding fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides. Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (I), the subscripts n and m respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one molecule of the alkoxyated fatty alcohol. The subscript k indicates the number of butylene oxide (BO) molecules or groups. The subscripts n, m, and k need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (I) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow, such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (I) must contain at least one ethoxy group. Preferably, the compound of formula I will also contain at least one propoxy group ( $C_3H_7O-$ ) or butoxy group ( $C_4H_9O-$ ). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (I) will have a value for m ranging from about 1 to about 10 with k zero or a value for k ranging from about 1 to about 10 with m zero. Most preferably, m will be about 1 to about 10 and k will be zero.

- 5 Other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 2 to about 5, and m being about 3 or about 4 with k zero. It is particularly advantageous to  
10 establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (I) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

- Additional preferred compounds for use in the invention having formula (I) above will have alkyl radicals containing about 12 to about 18 carbon atoms,  
15 or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

- Used as thinners according to the method of the invention, the compounds of formula (I) reduce the viscosity or lower the yield point of the drilling fluid to which they are added. These thinners are particularly effective  
20 at low temperatures, i.e., temperatures at or below about 50°F (about 10°C) and most particularly effective at temperatures at or below about 40°F (about 4°C). The lower limit of effectiveness for these thinners is about 14°F (about -10°C). The thinners do not significantly influence or affect the rheology of drilling fluids at high temperatures, particularly temperatures ranging from about  
25 100 to about 250° F or more.

The compounds of formula (I) are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

- Example drilling fluids comprising invert (water-in-oil) emulsions of  
30 particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and



polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at  
5 temperatures above about 32°F (about 0°C) or at least as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

10

- (a) most preferably, carboxylic esters of the formula:



where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 5 to about 23 carbon atoms and R'' is an  
15 alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 22 carbon atoms;

15

- (b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;

20

- (c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (d) water-insoluble alcohols of the formula:



where R''' is a saturated, unsaturated, linear or branched alkyl  
25 radical having about 8 to about 24 carbon atoms; and

25

- (e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis;  
30 European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic

diesters). Carboxylic esters of formula (II) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

- 5           In a preferred embodiment of this invention, compounds of formula (I) are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (II) where the radical R' in formula (II) is an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms).
- 10          Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.

- 15           For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.
- 20

- The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50 % by volume of one or more preferred compounds (a) – (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.
- 25

- Water is preferably present in the liquid phase of the drilling fluids used in the invention, and preferably in amounts not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, thinners of formula (I) are added to drilling fluids comprising invert emulsions containing about 15 to about 35% by volume water and more
- 30

preferably 20% by volume water and about 80% by volume oil phase. To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts and/or sodium salts.  $\text{CaCl}_2$  in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following rheology: plastic viscosity (PV) in the range of about 10 to about 60 cP, and preferably in the range of about 15 to about 40 cP, and yield point (YP) in the range of about 5 to about 40 lb/100 ft<sup>2</sup>, and preferably in the range of about 10 to about 25 lb/100 ft<sup>2</sup>, at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F (about 4°C), the YP should not exceed about 75 lb/100 ft<sup>2</sup>, and should preferably be in the range of about 10 to about 65 lb/100 ft<sup>2</sup>, more preferably about 15 to about 45 lb/100 ft<sup>2</sup>, and most preferably less than about 35 lb/100 ft<sup>2</sup>. A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft<sup>2</sup>.

Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA), incorporated herein by reference.

The solids content (not including low gravity solids), or the amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids, or weighting agents, which serve to increase the density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly.

Drilling fluids used in this invention may optionally also contain other additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO<sub>2</sub> and H<sub>2</sub>S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids range from about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize invert emulsions of the drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S. Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added. Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

Although the invention has primarily been described in the context of a method of using compounds of formula (I) as thinners for drilling fluids at low temperatures, the compounds of formula (I) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids at low temperatures.

Further description and use of the invention is shown by the following examples:

### Examples

To show the effect of the invention, the following experiments were conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

---

Ester	bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
CaCl <sub>2</sub> x 2 H <sub>2</sub> O	lb	27.2
Barite	lb	314.0
Dispersing auxiliary	lb	0.5

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Thinner	lb/bbl	2.0
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The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid  
 5 Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and with a C<sub>12/14</sub> fatty alcohol sulfate + 2 EO, sodium salt (C2), with a C<sub>12</sub> ether sulfate, sodium salt (C3) and with an oleic acid sulfonate disodium salt (C4), respectively, as prior art thinners, and comparison was made with these  
 10 thinners and with compounds of formula (I) in accordance with the invention. The formula (I) compounds used for this purpose were as follows:

- |       |  |
|-------|--|
| E1    | C12/C14 fatty alcohol containing 2 EO and 4 PO |
| E2    | C12/C14 fatty alcohol containing 5 EO and 4 PO |
| 15 E3 | C12/C18 fatty alcohol containing 5 EO and 4 PO |
| E4    | C12/C14 fatty alcohol containing 6 EO and 4 PO |

The invert muds were prepared in a conventional manner and subsequently, at 40°F and 122°F, the rheological characteristics of plastic  
 20 viscosity (PV) and yield point (YP) and the gel strength after 10 seconds and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.

Measurements E5, E6 and E7 were carried out using the thinners E1, E2 and E4, but in contrast to the details above, 45 lb of solids (rev dust, i.e., filter ash) were also added to each of the muds, in order to demonstrate the advantageous action of the compounds of formula (I) used in accordance with the invention in the case of high solids loading of the emulsions. In these cases, the measurements were taken only after 16 hours of aging at 150°F. The thinner was not added to the muds E5 to E7 until after aging.

The results of the measurements are given in Tables 1a and 1b below:

HALB016

Table 1a

	C1	C1	C2	C2	C3	C3	C4	C4	E1	E1	E2	E2	E3	E3	E4	E4
Temp. °F	40	122	40	122	40	122	40	122	40	122	40	122	40	122	40	122
PV (cP)	94	28	105	30	n.m.	33	91	24	93	31	87	28	94	28	83	29
YP lb/100 ft <sup>2</sup>	68	29	71	35	n.m.	62	69	20	70	41	34	33	62	41	30	30
Gels 10"/10'	27/29	12/13	24/29	15/15	n.m.	26/31	25/25	6/7	25/28	17/18	11/13	14/16	20/24	17/18	8/11	13/14

n.m.: not measurable

Table 1b - Measurements with addition of 45 lb rev dust

	C1	C1	E5	E5	E6	E6	E7	E7
Temperature °F	40	122	40	122	40	122	40	122
PV (cP)	94	28	107	37	108	40	106	37
YP lb/100 ft <sup>2</sup>	68	29	37	23	72	42	46	30
Gels 10"/10'	27/29	12/13	12/14	7/9	26/30	14/18	17/19	12/14

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the compounds of formula (I) used in the method and in the emulsions of the invention, especially at low temperatures, in comparison to the prior art. The higher plastic viscosity for E5 to E7 is attributable to the higher proportion of solids in the mud systems.

Further experiments may be seen in Tables 2 to 9. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. This illustrates particularly well the advantageous influence of the compounds of formula (I) on the rheology at low temperatures (40°F, 4°C) without any marked influence at high temperatures (120°F, 50°C). The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

In Tables 2 to 9:

PETROFREE LV® is 2-ethylhexyl octanoate (from Cognis, Germany)

PETROFREE LE® is linear alpha-olefin (from Cognis, Germany)

PETROFREE® is C8-14 fatty acid 2-ethylhexyl ester (from Cognis, Germany)

GELTONE II® is organophilic bentonite (from Baroid, Houston, Texas)

Thinner E1 is Formula I C12/C14 fatty alcohol of the invention containing 2 EO and 4 PO

Thinner E2 is Formula I C12/C14 fatty alcohol of the invention containing 5 EO and 4PO



Table 2

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids					
E2, lb/bbl	0		3		5	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	113	34	107	35
Yield point, lb/100ft <sup>2</sup>	38	14	25	14	19	13
10 sec gel, lb/100ft <sup>2</sup>	16	6	10	6	6	6
10 min gel, lb/100ft <sup>2</sup>	22	11	13	8	9	8
Fann 35 dial readings						
600 rpm	274	94	251	82	233	83
300 rpm	156	54	138	48	126	48
200 rpm	114	40	97	35	88	35
100 rpm	70	25	56	22	49	22
6 rpm	17	6	10	7	7	6
3 rpm	14	5	7	6	5	5

Table 3

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Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	126	50
Yield point, lb/100ft <sup>2</sup>	230	152	19	125
10 sec gel, lb/100ft <sup>2</sup>	108	64	10	50
10 min gel, lb/100ft <sup>2</sup>	110	66	13	52
Fann 35 dial readings				
600 rpm	590	254	271	225
300 rpm	410	203	145	175
200 rpm	336	179	103	149
100 rpm	248	146	59	119
6 rpm	112	79	10	62
3 rpm	100	70	8	58

Table 4

Mud system	PETROFREE LV			
Mud weight, lb/gal	16.0			
Oil/water ratio	80/20			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	152	51	142	40
Yield point, lb/100ft <sup>2</sup>	62	27	40	19
10 sec gel, lb/100ft <sup>2</sup>	22	10	18	10
10 min gel, lb/100ft <sup>2</sup>	48	26	22	12
Fann 35 dial readings				
600 rpm	366	129	324	99
300 rpm	214	78	182	59
200 rpm	158	59	130	45
100 rpm	98	38	78	30
6 rpm	24	11	16	10
3 rpm	20	9	12	9

Table 5

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Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	88	29
Yield point, lb/100ft <sup>2</sup>	54	53	37	53
10 sec gel, lb/100ft <sup>2</sup>	33	23	13	26
10 min gel, lb/100ft <sup>2</sup>	38	27	17	30
Fann 35 dial readings				
600 rpm	318	115	213	111
300 rpm	186	84	125	82
200 rpm	139	71	90	70
100 rpm	91	54	56	55
6 rpm	35	25	15	28
3 rpm	32	21	13	25

Table 6

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	113	34
Yield point, lb/100ft <sup>2</sup>	90	47	73	44
10 sec gel, lb/100ft <sup>2</sup>	38	21	27	20
10 min gel, lb/100ft <sup>2</sup>	44	24	30	22
Fann 35 dial readings				
600 rpm	310	115	299	112
300 rpm	200	81	186	78
200 rpm	157	67	142	64
100 rpm	110	50	95	48
6 rpm	42	23	31	22
3 rpm	38	21	27	19

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Table 7

Mud system	PETROFREE LE			
Mud weight, lb/gal	16.4			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	173	40	107	43
Yield point, lb/100ft <sup>2</sup>	21	9	18	7
10 sec gel, lb/100ft <sup>2</sup>	16	8	11	8
10 min gel, lb/100ft <sup>2</sup>	19	11	15	11
Fann 35 dial readings				
600 rpm	367	89	232	93
300 rpm	194	49	125	50
200 rpm	135	35	88	37
100 rpm	74	22	50	22
6 rpm	12	5	9	6
3 rpm	10	4	7	5

Table 8

Mud system	PETROFREE LE			
Mud weight, lb/gal	11.6			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	80	31	56	32
Yield point, lb/100ft <sup>2</sup>	25	18	27	16
10 sec gel, lb/100ft <sup>2</sup>	12	8	17	9
10 min gel, lb/100ft <sup>2</sup>	20	11	23	11
Fann 35 dial readings				
600 rpm	185	80	139	80
300 rpm	105	49	83	48
200 rpm	77	37	63	37
100 rpm	46	24	43	24
6 rpm	11	7	14	8
3 rpm	9	6	13	7

Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	113	35
Yield point, lb/100ft <sup>2</sup>	38	14	41	16
10 sec gel, lb/100ft <sup>2</sup>	16	6	16	9
10 min gel, lb/100ft <sup>2</sup>	22	11	20	11
Fann 35 dial readings				
600 rpm	274	94	267	86
300 rpm	156	54	154	51
200 rpm	114	40	114	39
100 rpm	70	25	71	26
6 rpm	17	6	18	8
3 rpm	14	5	14	8

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described composition and method can be made without departing from the intended scope of this invention as defined by the appended claims.

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We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid comprising an invert emulsion, said method comprising adding to said drilling fluid or well service fluid a compound having the formula:



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

2. The method of claim 1 wherein in said formula, k is zero and m is a number ranging from about 1 to about 10, or m is zero and k is a number ranging from about 1 to about 10.

3. The method of claim 1 wherein in said formula, n is a number ranging from about 1 to about 6, m is a number ranging from about 1 to about 6, and k is zero.

4. The method of claim 1 wherein said invert emulsion comprises a continuous oil phase comprising compounds or compositions flowable and pumpable at temperatures at least as low as about 40 degrees Fahrenheit.

5. The method of claim 1 wherein said invert emulsion comprises a continuous oil phase comprising compounds or compositions flowable and pumpable at temperatures above about 32 degrees Fahrenheit.

6. The method of claim 5 wherein said oil phase comprises compounds or compositions selected from the group comprising:

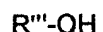
- (f) carboxylic esters of the formula:



where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

- (g) linear or branched olefins having about 8 to about 30 carbon atoms;  
(h) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (i) water-insoluble alcohols of the formula:



where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

- (j) carbonic diesters.

7. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said drilling fluid or well service fluid.

8. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said drilling fluid or well service fluid at temperatures less than about 50 degrees Fahrenheit.

9. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said drilling fluid or well service fluid.

10. The method of claim 1 wherein said compound reduces the viscosity of said

drilling fluid or well service fluid at low temperatures.

11. The method of claim 10 wherein said compound does not significantly affect the viscosity of said fluid at high temperatures.

12. The method of claim 1 wherein said compound is added to said fluid when said fluid is prepared.

13. The method of claim 1 wherein said compound is added to said fluid while said fluid is circulating in a wellbore.

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and a compound having the formula:



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

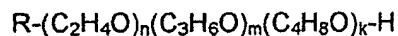
15. The drilling fluid or well service fluid of claim 14 wherein said compound is added in sufficient amounts to reduce the viscosity of said fluid at low temperatures.

16. The drilling fluid or well service fluid of claim 14 having a density of from about 8 to about 18 lbs/gal.



17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft<sup>2</sup> at about 40°F.

5 18. A method of reducing the viscosity of an invert emulsion drilling fluid or well service fluid at low temperatures comprising adding to said fluid an effective amount of compound having the formula:



10 where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

15 19. The method of claim 18 wherein said compound does not significantly affect the viscosity of the drilling fluid at high temperatures.

20. The method of claim 18 further comprising circulating said fluid in a wellbore and adding said compound to said fluid during said circulation.

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21. The method of claim 18 further comprising preparing said fluid and adding said compound to said fluid during said preparation.

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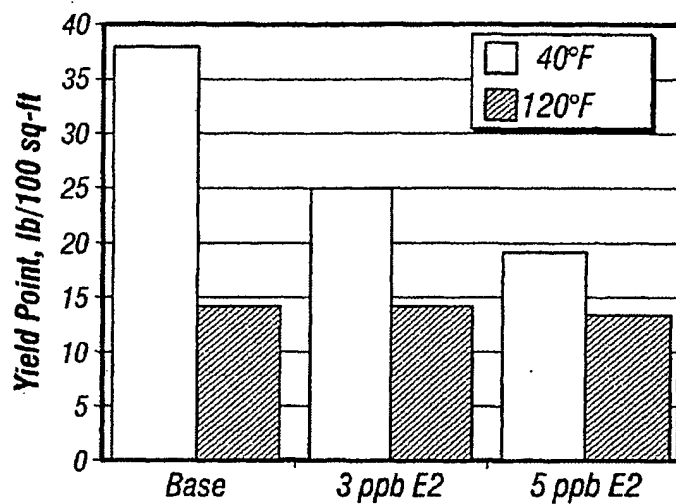


FIG. 1

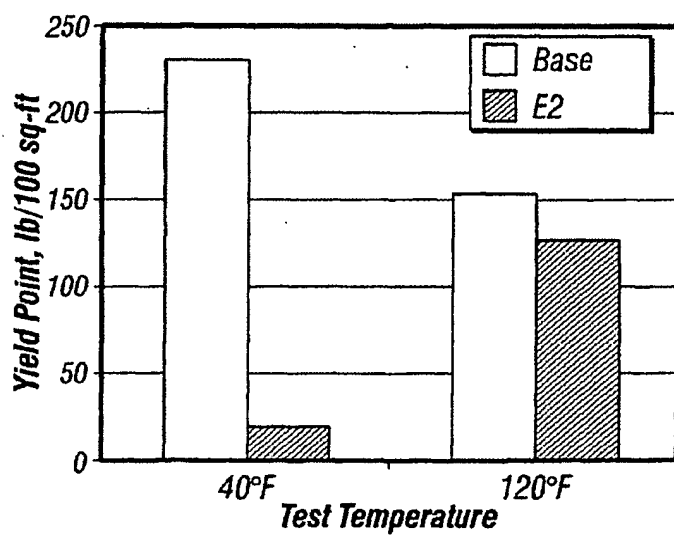


FIG. 2

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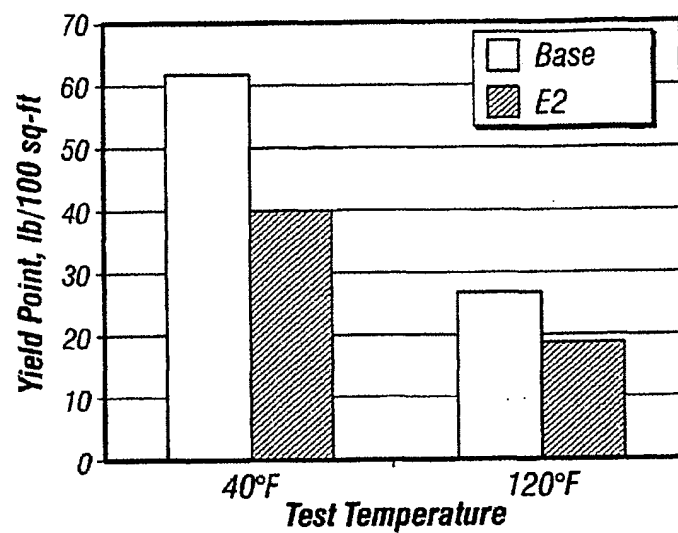


FIG. 3

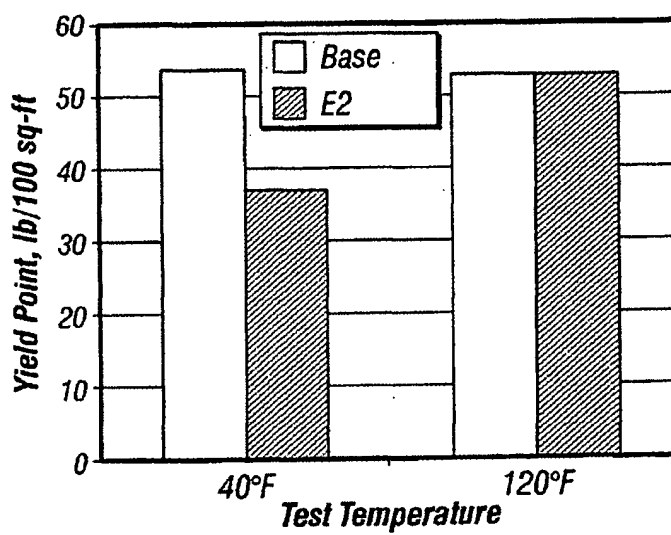


FIG. 4

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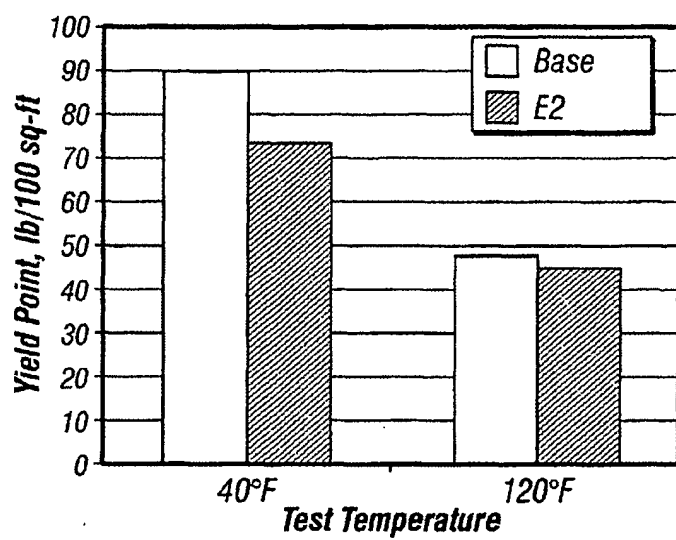


FIG. 5

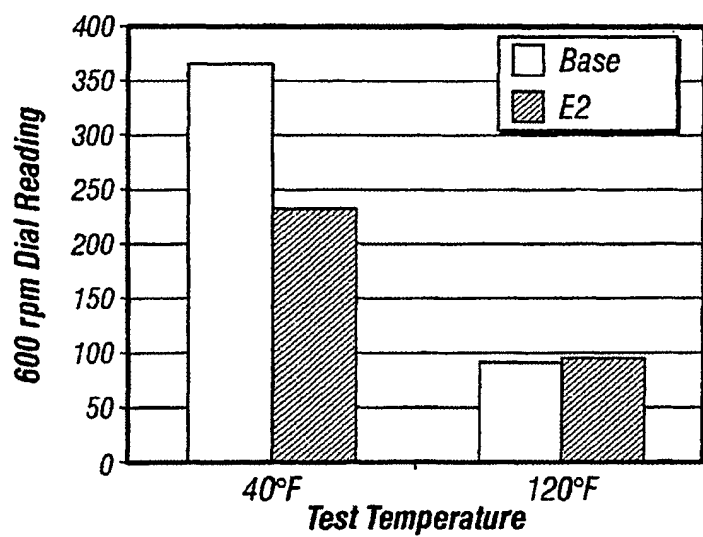


FIG. 6

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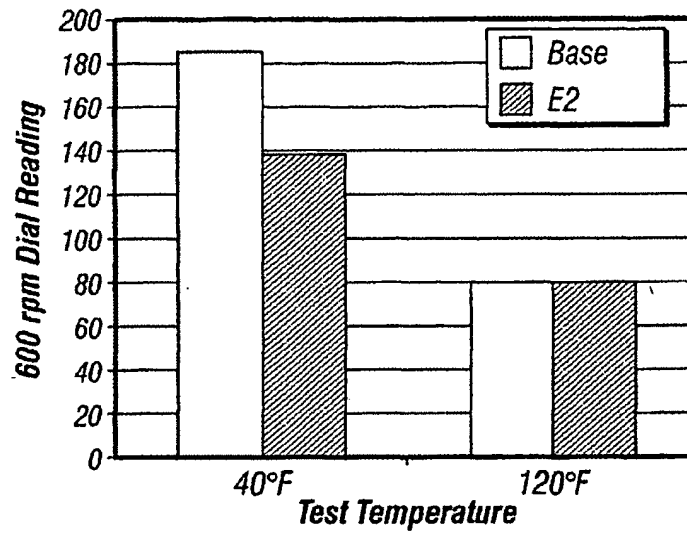


FIG. 7

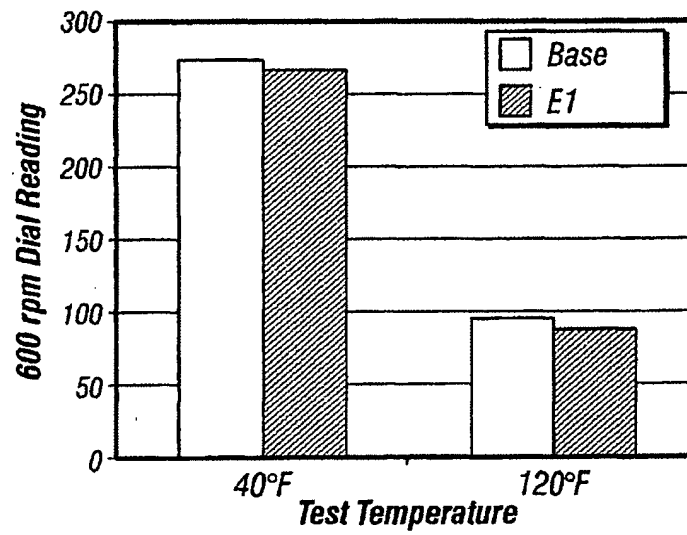


FIG. 8

# INTERNATIONAL SEARCH REPORT

Inte Application No  
PCT/US 00/35609

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09K7/06 E21B33/13

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 71241 A (RHODIA ;PROCTER & GAMBLE (US)) 30 November 2000 (2000-11-30) page 2, line 7 page 49, line 11 - line 22 page 5, line 3 - line 20 page 79, line 10 - line 26 page 86, line 22 - line 29; claim 12	1, 2, 4-21
Y	---	3
X	EP 0 561 608 A (LUBRIZOL CORP) 22 September 1993 (1993-09-22) page 13, line 39 -page 14, line 6 page 17, line 20 -page 19, line 16; claims 1-25	1, 2, 4-21
Y	---	3
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 March 2001

Date of mailing of the international search report

12/04/2001

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 Inter application No  
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 330 662 A (JAHNKE RICHARD W ET AL) 19 July 1994 (1994-07-19) column 22, line 15 -column 23, line 15 column 28, line 47 -column 29, line 16; claims 1-51	1,2,4-21
Y	---	3
X	US 6 090 754 A (CHAN ALBERT F ET AL) 18 July 2000 (2000-07-18) column 1, line 17 -column 3, line 13 column 5, line 8 - line 15 column 6, line 62 -column 8, line 40; claims 1-14	1,2,4-21
Y	---	3
X	WO 99 50370 A (KESAVAN SUBRAMANIAN ;BJ SERVICES CO (US); LE HOANG V (US); DAWSON) 7 October 1999 (1999-10-07) page 12, line 5 -page 13, line 11; example 5	1,2,4-21
A	--- "Neodol 23-6.5" SHELL CHEMICALS, 'Online! XP002164096 Retrieved from the Internet: <URL:http://www.shellchemicals.com/neodol/ 1,1098,876,00.html> 'retrieved on 2001-03-28! page 1 -page 2	1-21
A	--- "Altonic product sheet" CONDEA, 'Online! XP002164097 Retrieved from the Internet: <URL:http://www.condea.de/products/surfact ants/surfactants_nonionic/alfonic.html> 'retrieved on 2001-03-28! page 1 -page 4	1-21
A	--- "Tergitol detergents" SIGMA PRODUCT INFORMATION SHEET, 'Online! XP002164098 Retrieved from the Internet: <URL:http://www.sigald.sial.com/sigma/prod data/t7543x.htm> 'retrieved on 2001-03-28! page 1 -page 2	1-21
Y	--- US 6 001 790 A (HINGERL MANUELA ET AL) 14 December 1999 (1999-12-14) examples 1-8	3
Y	--- US 5 403 508 A (KUNZ WALTER ET AL) 4 April 1995 (1995-04-04) examples 1-4	3
	---	

-/--

## INTERNATIONAL SEARCH REPORT

Intern .pplication No  
PCT/US 00/35609

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 308 401 A (GEKE JUERGEN ET AL) 3 May 1994 (1994-05-03) example 1 -----	3



# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter Application No

PCT/US 00/35609

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0071241 A	30-11-2000	AU 5044800 A	12-12-2000
EP 0561608 A	22-09-1993	US 5283235 A	01-02-1994
		CA 2091419 A	18-09-1993
		CN 1077212 A	13-10-1993
		FI 931161 A	18-09-1993
		ZA 9301870 A	06-10-1993
		AU 3522293 A	06-01-1994
		BR 9300848 A	25-01-1994
		MX 9301445 A	31-01-1994
		NO 930952 A	03-01-1994
US 5330662 A	19-07-1994	CA 2091420 A	18-09-1993
		CN 1076471 A	22-09-1993
		EP 0561607 A	22-09-1993
		FI 931163 A	18-09-1993
		NO 930950 A	20-09-1993
		US 5620946 A	15-04-1997
		ZA 9301864 A	05-10-1993
US 6090754 A	18-07-2000	US 5830831 A	03-11-1998
		EP 1051237 A	15-11-2000
		WO 9929408 A	17-06-1999
		NO 20002949 A	26-07-2000
WO 9950370 A	07-10-1999	AU 3354899 A	18-10-1999
		GB 2342657 A	19-04-2000
US 6001790 A	14-12-1999	DE 19652680 A	25-06-1998
		AU 5856598 A	15-07-1998
		WO 9827188 A	25-06-1998
		EP 0946697 A	06-10-1999
		HU 0000595 A	28-07-2000
US 5403508 A	04-04-1995	AT 130362 T	15-12-1995
		DE 59300931 D	21-12-1995
		EP 0569843 A	18-11-1993
		ES 2081657 T	01-03-1996
		JP 6032731 A	08-02-1994
US 5308401 A	03-05-1994	DE 4014859 A	14-11-1991
		AT 116681 T	15-01-1995
		AU 7769091 A	27-11-1991
		CA 2082517 A	10-11-1991
		DE 59104163 D	16-02-1995
		DK 527824 T	19-06-1995
		WO 9117233 A	14-11-1991
		EP 0527824 A	24-02-1993
		ES 2066441 T	01-03-1995
		PT 97594 A, B	28-02-1992